

電子ビームリソグラフィのためのマイクロ近接電子源

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号	52
学位授与番号	3860
URL	http://hdl.handle.net/10097/37576

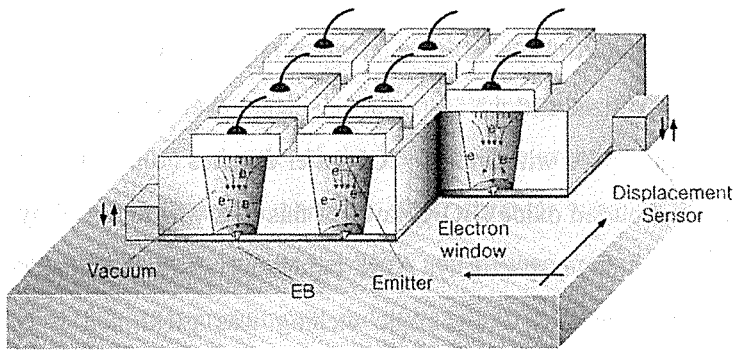
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授 与 学 位	博士 (工学)
学 位 授 与 年 月 日	平成19年9月12日
学位授与の根拠法規	学位規則第4条第1項
研究科, 専攻の名称	東北大学大学院工学研究科 (博士課程) ナノメカニクス専攻
学 位 論 文 題 目	電子ビームリソグラフィのためのマイクロ近接電子源
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論 文 内 容 要 旨

Electron sources have been used for versatile applications, such as electron microscopy, electron beam lithography, X-ray radiation, and visual displays, etc. CRT monitors are the friendliest machines in our lives for several decades. Scanning electron microscopy using the secondary electrons has become the most useful tool for analyzing micro sample. Also application to next generation data storage was reported by some researchers. In general, the use of high-energy electron sources is limited to vacuum conditions. Therefore, electron windows have been investigated for application to an electron source, in order to provide electrons in atmospheric conditions. Electron windows made of a thin membrane can partially transmit high-energy electrons from a vacuum to the atmosphere. Owing to this characteristic, electron windows have been developed for energy dispersive X-ray spectroscopy and scanning electron microscopy (SEM) in atmospheric applications for portability and interplanetary exploration.

Electron beam lithography with high production throughput is of considerable practical concern, due to recent developments in nanofabrication technology. In principle, electron beam lithography can define fine features that are smaller than that using optical lithography, but the throughput is quite low in the case of nanometer size features. Nanoimprint lithography has the capability of defining sub-micrometer patterns, but electron beam lithography is generally required for manufacturing the mold used for nanoimprint lithography. One of the critical issues of electron beam lithography is its low production throughput. In order to improve the throughput, multi-beam lithography has been proposed, but many difficulties associated with the complexity of the multi-beam system have to be solved.

We propose the miniature proximity electron source which can be used to emit electrons into the atmosphere from an emitter via electron windows of sub-micrometer to nanometer size. The emitted electrons will be absorbed by the air; therefore, the device is used within a range proximate to the target material. The size of the electron window is much smaller than that of a conventional electron window, and consequently a small beam



near the electron window can be formed easily without complex electron optics. Electrons are field-emitted from the emitters and accelerated by applying a high voltage between a cathode and anode. A portion of the electrons then pass through the thin membrane and are emitted into the atmospheric environment. The diameter of

the emitted electron beam will depend on the aperture size. Figure shows the concept of electron source with electron window. Displacement sensors will control the gap of the device and a target and the throughput will be progressed by array.

The electron window should be very thin membrane to transmit electron from vacuum to atmosphere. The maximum penetration depth of the electrons, R , into a solid state material depends on the density of the solid and is given by $R = 4E^2 / c_T \rho m^2$, where E is the electron energy, $c_T (=5.05 \text{ m}^6/\text{kg}\cdot\text{s}^4)$ is the Thomson-Whiddington coefficient, ρ is the density, and m is the electron rest mass. Thus, low density materials are suitable for electron-permeable windows. In addition, this equation can apply to gas atmospheres. The penetration depth of the ambient atmosphere is approximately 1900 times longer than that of silicon. In order to increase the electron transmittance, the thickness of the electron windows should be as thin as possible.

Transparency for electron, mechanical robustness and easiness for the fabrication are required for the material of the electron window. As the candidates of electron window, silicon carbide (SiC), silicon nitride (Si₃N₄) and diamond-like carbon were considered. SiN was applied to the electron windows with a cathode ray tube by Hanlon, et al. two decades ago. Recently, Si₃N₄ window for MEMS electron source was reported. However, according to recent report, silicon nitride is melted in high energy range due to its low thermal conductivity.

In this study, we employed single-crystalline silicon (Si) as the material for the electron windows, owing to its high permeability and ease of fabrication in producing an ultra-thin Si structure. The thermal conductivity of Si is three times of that of SiN. Si micro- and nano-structures can now be fabricated due to recent advances in micro fabrication technology. In addition, single crystalline silicon has high robustness and low residual stress. Micro- and nano-electron windows were fabricated by micro fabrication technology.

As the field emitter, several materials are under investigation, e.g., silicon, diamond, carbon nano tubes (CNTs), etc. Especially, carbon nano tubes are considered as a promising material for the field emitter, and could be grown selectively on catalyst films by chemical vapor deposition. According to latest reports, carbon nano coils (CNCs) show excellent field emission properties as well as that of carbon nano tubes, and can be also selectively grown on Fe and indium tin oxide (ITO) films. The ITO film will make good electronic contact between carbon nano coil emitters and a silicon substrate, which is desirable for field emission devices. In these reasons, carbon

nano coils were chosen as an emitter material of the device.

For the fabrication of anode and silicon electron window, two silicon-on-insulator (SOI) wafers were used. One SOI wafer with 150-nm-thick top silicon layer was oxidized and the 50-nm-thick silicon layer was obtained. This layer will be the electron window. The wafer was bonded with another SOI wafer that has (100)-oriented top silicon layer with 7- μm -thick. A handling layer and buried oxide (BOX) layer of this SOI was removed by ion reactive etching (RIE) and buffered-HF (BHF) solution, respectively. After oxidation, a silicon dioxide pattern with $9 \times 9 \mu\text{m}^2$ square was defined by photolithography. Anisotropic etching was performed in a tetramethyl ammonium hydroxide (TMAH) solution and an inversed-pyramidal pit was formed on the top silicon layer. After wet-oxidation at 950°C , the oxide layer was slightly etched in BHF solution. In this step, a small hollow was formed at the bottom of the inversed-pyramidal etch pits. Ion reactive etching (RIE) was performed to make a narrow aperture, and the oxide layer was removed in BHF. Consequently we obtained the apertures of about 700 nm and 250nm diameter. Subsequently, the substrate was anodically bonded with a Pyrex glass in which through-holes were formed by sandblast. The handle silicon and BOX layers of the SOI wafer were completely removed.

For the selective growth of carbon nano coils on a catalytic metal film, thermal chemical vapor deposition (CVD) was employed. After patterning by photolithography on a silicon substrate, 200-nm-thick ITO and 15-nm-thick Fe films were formed on the silicon substrate. Subsequently lift-off process was conducted and the patterned metal film was obtained. The growth was done at 700°C in atmospheric pressure. In advance, pure argon (Ar) was flowed into a quartz furnace until reaching the target temperature. Then, a mixture of Ar (45ml/min) and acetylene (C_2H_2) (150ml/min) gases was introduced in the furnace and the growth was started. Consequently, many Carbon nano coils were grown on the patterned substrate. Coil diameters of carbon nano coils were ranging from about 100 nm to 2 μm . Anodic bonding of the Pyrex glass and the cathode layer was performed in vacuum.

The field emission characteristics of the carbon nano coils were measured in an ultra high vacuum chamber. When a voltage was applied between the anode and the emitter, the current flowing into the anode was measured. The measured emission current followed the Fowler-Nordheim (F-N) mechanism for field emission.

The electron transmission of an array of 5×5 electron windows with a window size of $1.5 \times 1.5 \mu\text{m}$ was also evaluated. A conductive phosphor screen was placed above the electron windows at a distance of 2 mm. A voltage of 3 kV was applied between the carbon nano coils cathode and anode. An additional voltage of 100 V was also applied to the phosphor screen against the anode, and the transmitted electron current was measured from the current flowing into the screen. It is found that approximately 4% of the electrons emitted from the carbon nano coils are transmitted through the electron window. From this current, the transmitted beam current density at the electron window is calculated to be $90 \text{ pA}/\mu\text{m}^2$. Next, the transmittances of individual electron windows were evaluated using SEM.

The windows without emitters were placed in a SEM chamber and an electron beam was focused onto one of the grounded electron windows. The electrons transmitted via the electron window were then measured with a Faraday cup. The primary electron current was also measured using the Faraday cup. The transmittance can be calculated from the ratio of the transmitted current to the primary electron beam current. Measurements were performed on various samples with different window thicknesses. In the case of thickness of 50 nm, transmittance was saturated at 85 % and voltage around 10 kV. It can be seen that the thinner electron windows exhibit higher transmittance, and quite high transmittance was obtained even at low acceleration voltages. As the reason that the curve did not go 100%, backscattering and absorption in the window could be considered.

Electron beam lithography was then demonstrated using the array of 5×5 electron windows with a size of 1.5×1.5 μm and a thickness of 50 nm. A 350 nm thick positive electron beam resist (ZEP520A) was spin-coated on a silicon substrate and the electron windows were contacted with the substrate in a SEM chamber. The accelerated electron beam was scanned on the electron window array, and the resist was exposed to the electron beam transmitted through the electron windows. In the cases of acceleration voltage of 10 kV and exposure times of 1 and 3 min, patterns of electron windows of the transferred on the resist. When the primary beam current was 46 pA, the average current density was 3.7 fA/ μm^2 . If 80 % of the electrons are transmitted, then the total dose corresponds to 18 $\mu\text{C}/\text{cm}^2$ for the case of a 1 min exposure time. From previous experimental results of the transmittance from CNC emitters, it was determined that a beam current 24,000 times larger can be achieved if nano coil emitters are used. In addition, the size of the electron windows can be reduced by using a low temperature for the oxidation of Si and etching techniques.

Monte Carlo simulation was performed on a model of multi-layers with 50-nm-thick Si membrane, 100 nm air gaps, 350 nm thick resist on a silicon substrate. A primary electron beam with a diameter of 50 nm and energy of 10 keV is irradiated onto the Si membrane. Electrons are slightly scattered and spread in the membrane. However, electron scattering in the air gap is negligible if the gap is enough small. Thinner membrane can reduce the electron scattering and makes electron distribution in the resist small. From a technical point of view, each emitter can be electrically isolated and individually operated. It is expected that this electron window device can be applied to high-throughput electron beam nanolithography in ambient atmosphere with scanning of the substrate with a small gap.

論文審査結果の要旨

半導体微細加工技術を発展させたマイクロマシニング技術を用いると、小型の要素を集積化し、従来にはない新しい機能が実現できる。

本論文は、カーボンナノ材料を用いたエミッタとマイクロマシニングにより作製した極薄の微小シリコン膜からなる電子透過膜から構成される電子源、および電子源のリソグラフィへの応用に関する研究をまとめたもので、全編8章よりなる。

第1章は序論であり、研究背景について述べられている。また、これまでに報告されている電子源や電子透過膜について比較検討し、エミッタの種類について分類して本論文の位置付けに関して議論している。

第2章では、電子を放出するエミッタを分類し、それらの原理についてまとめている。

第3章では、固体と電子の相互作用や電子透過膜中での電子の散乱理論について述べている。また、様々な材料の電子透過特性について考察し、シリコンの場合について理論的に検討している。

第4章では、エミッタとして利用するカーボンナノチューブやカーボンナノコイルの構造、物性や歴史について述べられている。

第5章では、本論文で提案するデバイスの原理と構造について述べられている。本デバイスは、真空封止されたカーボンナノコイルのエミッタから電子を放出し、サブミクロンの大きさの電子透過窓を透過させて大気中に放出できる構造を持っている。

第6章は、デバイスの作製方法と作製結果についてまとめたものである。カーボンナノコイルは、ITOと鉄触媒をパターニングしたシリコン基板上に熱化学気相堆積法で成長させた。デバイスは低温酸化により形成した酸化膜の厚さが形状に依存して薄く、少しエッチングすると穴が開くことを利用して形成した独創的なものである。

第7章は、デバイスの評価方法とその結果、およびリソグラフィへの応用についてまとめたものである。作製したカーボンナノコイルやカーボンナノチューブの電界放出特性を評価した。また、微小の電子透過膜の電子の透過率を実験的に求め、モンテカルロシミュレーションによる値と比較している。電子線レジストをコートしたシリコン基板に電子透過膜を透過した電子を利用してパターンを形成したことが述べられている。電界レンズなど複雑な電子光学系を必要とせずに、小さな電子ビームが得られる特徴がある。

第8章は結論である。

以上、要するに本論文は、新しい電子源の概念と構造を提案し、独自の作製技術により作製し、ナノリソグラフィに応用できることを実験と理論の両面から示したもので、ナノメカニクスと微細加工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。